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(54) Title: WATER-DISPERSIBLE GRANULAR AGRICULTURAL COMPOSITIONS MADE BY HEAT EXTRUSION

(57) Abstract

Rapidly disintegrating water-soluble or water-dispersible granular compositions are made by extruding a premix through a die or screen at elevated temperature. The extruded composition is chopped or milled to form a granular product. The compositions contain one or more water-soluble ingredients which soften or melt at elevated temperatures. No water is added in the process thereby eliminating the need for drying.

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TITLE

WATER-DISPERSIBLE GRANULAR AGRICULTURAL COMPOSITIONS MADE BY HEAT EXTRUSION

BACKGROUND OF THE INVENTION

The present invention relates to water-dispersible granular compositions comprising active ingredients of value in agriculture.

It is advantageous to formulate active pesticides as water-dispersible compositions which can be readily mixed with water and applied by means of a spraying apparatus to a locus to be protected. It is also advantageous that such granular compositions can be readily dispersed or dissolved in water. It is also advantageous that the granular compositions have good attrition resistance, uniform size granules and uniform bulk density.

World Patent WO 89/00079 discloses an extrusion process to make water-dispersible granules of agricultural chemicals in which water is added to make an extrudable wet mix. The extrudate is rolled to break the product down to granules and then optionally dried.

U.S. 4,065,289 discloses a herbicidal composition containing a plant fertilizer component and a herbicide component which is extruded through a die at 70°C-145°C. The herbicide component acts as a lubricant to permit ready extrusion and to form a coherent extrudate.

SUMMARY OF THE INVENTION

The present invention is directed to rapidly disintegrating water-dispersible granular agricultural compositions comprising by weight based on the total weight of the composition:

1) 0.01-90% of one or more active ingredients;
2) 1-60% of one or more water-soluble diluents;
3) 0-30% of one or more water-soluble heat activated binders that melt at temperatures between 40 - 120°C; and
4) two or more additives selected from the group consisting of:
   a) 0-10% anticaking agent(s);
   b) 0-10% chemical stabilizer(s);
   c) 0-20% gas generating agents;
   d) 0.1-10% wicking or swelling disintegrant(s);
   e) 0.1-20% dispersant(s);
   f) 0-5% wetting agent(s); and
   g) 0-80% inert filler(s).

The sum of all ingredients in a composition is 100%.

The invention is also directed to a process for preparing the compositions of the invention, said process comprising extruding a premix through a die or screen at elevated temperature without using any water. Accordingly, the process of the invention comprises extruding a dry premix comprising by weight based on the total weight of the composition:

1) 0.01-90% of one or more active ingredients;
2) 1-60% of one or more water-soluble diluents;
3) 0-30% of one or more water-soluble heat activated binders that melt at temperatures between 40 - 120°C; and

4) two or more additives selected from the group consisting of:

(a) 0-10% anticaking agent(s);
(b) 0-10% chemical stabilizer(s);
(c) 0-20% gas generating agents;
(d) 0.1-10% wicking or swelling disintegrant(s);
(e) 0.1-20% dispersant(s);
(f) 0-5% wetting agent(s); and
(g) 0-80% inert filler(s);

through a die or screen at a temperature from 50°C to 130°C and chopping or milling the extruded material to form uniform granules.

The active ingredient is at least one chemical used for crop protection or plant growth regulation or pesticide. More specifically, ingredients are selected from the class of herbicides, fungicides, bactericides, insecticides, insect antifeedants, acaricides, miticides, nematocides, and plant growth regulants.

The preferred compositions of the invention are:

1. The composition of the general formula wherein the active ingredient(s) comprise 0.03-80%, the heat activated binder(s) comprise 1-15% and the water-soluble diluent(s) comprise 1-40% by weight based on the total weight of the composition.

2. The composition of Preferred 1 wherein the active ingredient(s) comprise 10-70% by weight.

3. The composition of Preferred 2 wherein the water soluble diluent is urea, ethylurea, sorbitol, lactose or sodium acetate trihydrate and mixtures of the foregoing.

4. The composition of Preferred 3 wherein the heat activated binder(s) is selected from the classes consisting of polyethoxylated alkylphenols and ethylene oxide/propylene oxide copolymers and mixtures of the foregoing.

5. The composition of Preferred 4 wherein the disintegrant(s) is cross-linked polyvinyl pyrrolidone or cross-linked sodium carboxymethyl cellulose.

6. The composition of Preferred 5 wherein the dispersant is a napthalene-sulfonate-formaldehyde condensate or a ligninsulfonate.

7. The composition of Preferred 4 wherein the heat activated binder(s) is a block copolymer of ethylene oxide/propylene oxide where 80% is ethylene oxide and 20% is propylene oxide, or polyethoxylated dinonylphenol with 150 ethylene oxide units.

8. The composition of Preferred 3 wherein the water soluble diluent is urea or sorbitol.

9. The composition of Preferred 8 wherein the active ingredient is N'(3,4-dichlorophenyl)-N,N-dimethyl urea (diuron).

10. The composition of Preferred 8 wherein the active ingredient is methyl 2-benzimidazole-carbamate (carbendazim).

11. The composition of Preferred 8 wherein the active ingredient is 3-cyclohexyl-6-dimethylamino-1-methyl-1,3,5-triazin-2,4-(1H,3H)dione (hexazinone).

12. The composition of Preferred 8 wherein the active ingredient is selected from:

methyl 2-[[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]benzoate;

methyl 3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]-sulfonyl]-2-thiophenecarboxylate;

2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]-benzene-sulfonamide;

ethyl 2-[[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]-sulfonyl]benzoate;

methyl 2-[[[[(4-methyl-6-methoxy-1,3,5-triazin-2-yl)amino]carbonyl]amino]-sulfonyl]benzoate;

2-[[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]-N,N-dimethyl-3-pyridinecarboxamide;

methyl 2-[[[[[4-ethoxy-6-(methylamino-1,3,5-triazin-2-yl]amino]carbonyl]-amino]sulfonyl]benzoate;

methyl 2-[[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N-methylamino]carbonyl]amino]sulfonyl]benzoate;

methyl 2-[[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-methyl]benzoate;

N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl]-3-(ethylsulfonyl)-2-pyridine sulfonamide;

methyl 2-[[[[[4,6-bis(difluoro-methoxy)-2-pyrimidinyl]amino]carbonyl]-amino]sulfonyl]benzoate;

2-(2-chloroethoxy)-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl]-benzene sulfonamide;

ethyl 5-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazole-4-carboxylate; or

N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl]-1-methyl-4-(2-methyl-2H-tetrazol-5-yl)-1H-pyrazole-5-sulfonamide.

DETAILED DESCRIPTION OF THE INVENTION

Compositions for agricultural or pesticidal use are usually manufactured and sold as liquid or solid concentrates. In recent years fromulations based on water-dispersible granules have become increasingly popular because they offer several advantages over other types of agricultural formulations. For example, they are stable during storage and transport. Often this is a concern with aqueous suspension concentrates that can settle or develop crystals in storage if the active ingredient has sufficient water solubility. Also, aqueous suspension concentrates are not suitable for active ingredients which are subject to aqueous hydrolysis. This is not a problem with water-dispersible granules. In comparison to wettable powders, water-dispersible granules are convenient to handle and measure and are relatively dust-free. They avoid the skin-toxicity and odor problems associated with solvent-based formualtions such as emulsion concentrates and organic suspension concentrates.

To make water-dispersible granules useful for application they are usually diluted in a mix tank containing water to form a solution or dispersion which can be sprayed. The dispersed particles formed on dilution should be no larger than 50 microns in their largest dimension to avoid nozzle pluggage or premature settling which results in uneven application of the pesticide. It is therefore

necessary that all of the components of the formulated product rapidly and completely disperse or dissolve in the dilution water.

Conventional methods for preparing water-dispersible granule compositions involve (1) water-spraying in fluidized bed or pan granulation equipment (2) spray-drying (3) dry compaction and (4) extrusion of a water-wet paste. Granules prepared by fluid-bed, spray-drying or pan granulation can be formulated to disperse rapidly when diluted in water. However these processes require specialized technology including extensive dust collection systems and a space-consuming and expensive drying operation. Dry compaction and extrusion generally do not produce fast-dispersing granules, and wet-extrusion also requires a drying step.

The present invention comprises water-dispersible granular compositions which are made by extruding a dry premix through a die or screen at elevated temperature and chopping or grinding the extruded material to form granules. Advantages of these heat extruded granular compositions include (1) rapid disintegration and good dispersion properties in water (2) good attrition resistance (3) more uniform size and bulk density than granules prepared by fluid-bed or pan granulation, or by other tumbling/mixing processes such as in a rotating drum granulator (4) a simple process which uses readily available commercial extruding equipment, and (5) no need for drying or dust collection equipment.

The compositions of this invention are prepared as follows. An extrudable premix is prepared by combining the pesticidal particles with one or more

water-soluble diluents, and preferably one or more water-soluble heat activated binders which soften or melt in the desired temperature range. Other additives included in the premix are wicking or swelling disintegrants and one or more dispersants. Particulate additives such as wetting agents, gas-generating agents, anticaking agents, chemical stabilizers, and inert fillers may optionally be added.

The process of the invention comprises extruding a dry premix comprising by weight based on the total weight of the composition:

1) 0.01-90% of one or more active ingredients;
2) 1-60% of one or more water-soluble diluents;
3) 0-30% of one or more water-soluble heat activated binders that melt at temperatures between 40-120°C; and
4) two or more additives selected from the group consisting of:
    a) 0-10% anticaking agent(s);
    b) 0-10% chemical stabilizer(s);
    c) 0-20% gas generating agents;
    d) 0.1-10% wicking or sweliling disintegrant(s);
    e) 0.1-20% dispersant(s);
    f) 0-5% wetting agent(s); and
    g) 0-80% inert filler(s);

through a die or screen at a temperature from 50°C to 130°C and chopping or milling the extruded material to form uniform granules.

The preferred embodiments of the process of the invention include the preferred conditions for the compositions recited above and a temperature of from 75°C to 115°C.

The premix is blended and milled to an average particle diameter between 1 and 50 microns. Preferably, the premix is fed or metered to an extruder that has been heated electrically, by steam, or by other conventional means of heating. Suitable extruders include axial and radial designs with single or twin screws, and roll-type extrusion presses. In some types of extrusion equipment, for example, a California Pellet Mill, the heat can be generated from friction. Other means of heating the premix could include preheating the premix before extrusion, or heating the individual components of the premix before blending. The premix is heated to or maintained at a temperature in the range of about 50°C to 130°C, preferably about 75°C to 115°C. The optimum temperature will vary with the composition, but can be determined empirically.

The heated premix is extruded through a die or screen. The die holes range in diameter from 0.25 mm to 7 mm, preferably from 0.4 mm to 2 mm. Depending on the composition and the type of extruder used, the extruded material might be recycled until the strands are uniform in texture. Generally the extruded material is allowed to cool to harden and reduce stickiness, although this may not be necessary. The strands are chopped, milled or rolled and then screened to approximately 10 to 60 U.S. mesh size granules. A narrower cut size range may be selected. In some cases the strands may be sufficiently brittle so that they break on their own into short lengths.

The active ingredient should be chemically stable in the extrusion temperature range. Examples of suitable active ingredients are listed in Table 1.

TABLE 1

HERBICIDES

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
1	acifluorfen	142-160	5-[2-chloro-4-(trifluoro methyl)phenoxy]-2-nitro-benzoic acid
2	asulam	142-144	methyl [(4-aminophenyl)-sulfonyl]carbamate
3	atrazine	175-177	6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine
4	bensulfuron methyl	185-188	2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl]amino]sulfonyl]-methyl]benzoic acid, methyl ester
5	bentazon	137-139	3-(1-methylethyl)-(1H)-2,1,3-benzothiadiazin-4(3H)-one, 2,2-dioxide
6	bromacil	158-159	5-bromo-6-methyl-3-(1-methyl-propyl)-2,4(1H,3H)pyrimi-dinedione
7	bromoxynil	194-195	3,5-dibromo-4-hydroxybenzo-nitrile

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
8	chloramben	200-201	3-amino-2,5-dichlorobenzoic acid
9	chlorimuron ethyl	>100	2-[[[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]benzoic acid, ethyl ester
10	chloroxuron	151-152	N'-[4-(4-chlorophenoxy)-phenyl]N,N-dimethylurea
11	chlorsulfuron	174-178	2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-amino]carbonyl]benzene-sulfonamide
12	chlortoluron	147-148	N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea
13	clomazone	oil	2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazoli-dinone
14	cyanazine	166-167	2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile
15	dazomet	104-105	tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
16	desmediphan	120	ethyl [3-[[(phenylamino)-carbonyl]oxy]phenyl]-carbamate
17	dicamba	114-116	3,6-dichloro-2-methoxybenzoic acid
18	dichlobenil	139-145	2,6-dichlorobenzonitrile
19	dichlorprop	117-118	(±)-2-(2,4-dichlorophenoxy)-propanoic acid
20	diphenamid	134-135	N,N-dimethyl-α-phenylbenzene-acetamide
21	dipropetryn	104-106	6-(ethylthio)-N,N'-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine
22	diuron	158-159	N'-(3,4-dichlorophenyl)-N,N-dimethylurea
23	thiameturon	>100	3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]-carbonyl]amino]sulfonyl]-2-thiophenecarboxylic acid, methyl ester

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
24	----	>100	2-[[[[N-(4-methoxy-6-methyl-1,3,5-triazine-2-yl)-N-methylamino]carbonyl]-amino]sulfonyl]benzoic acid, methyl ester
25	fenac	156	2,3,6-trichlorobenzeneacetic acid
26	fenuron	133-134	N,N-dimethyl-N'-phenylurea
27	fluometuron	163-164	N,N-dimethyl-N'-[3-(trifluoro-methyl)phenyl]urea
28	fluridone	151-154	1-methyl-3-phenyl-5-[3-(tri-fluoromethyl)phenyl]-4(1H)-pyridinone
29	fomesafen	220-221	5-[2-chloro-4-(trifluoro-methyl)phenoxy]-N-(methyl-sulfonyl)-2-nitrobenzamide
30	glyphosate	200	N-(phosphonomethyl)glycine
31	hexazinone	115-117	3-cyclohexyl-6-(dimethyl-amino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
32	imazamethabenz	>100	6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-m-toluic acid, methyl ester and 6-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)-p-toluic acid, methyl ester
33	imazaquin	219-222	2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-3-quinolinecarboxylic acid
34	imazethapyr	172-175	(±)-2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid
35	ioxynil	209	4-hydroxy-3,5-diiodobenzonitrile
36	isoproturon	155-156	N-(4-isopropylphenyl)-N',N'-dimethylurea
37	isouron	119-120	N'-[5-(1,1-dimethylethyl)-3-isoxazolyl]-N,N-dimethylurea
38	isoxaben	176-179	N-[3-(1-ethyl-1-methylpropyl)-5-isoxazolyl]-2,6-dimethoxybenzamide

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
39	karbutilate	176-178	3-[[(dimethylamino)carbonyl]-amino]phenyl-(1,1-dimethyl-ethyl)carbamate
40	lenacil	316-317	3-cyclohexyl-6,7-dihydro-1H-cyclopentapyrimidine-2,4-(3H,5H)dione
41	MCPA	100-115	(4-chloro-2-methylphenoxy)-acetic acid
42	MCPB	100	4-(4-chloro-2-methylphenoxy)-butanoic acid
43	mefluidide	183-185	N-[2,4-dimethyl-5-[[(tri-fluoromethyl)sulfonyl]-amino]phenyl]acetamide
44	methabenz-thiazuron	119-120	1,3-dimethyl-3-(2-benzothia-zolyl)urea
45	methazole	123-124	2-(3,4-dichlorophenyl)-4-methyl-1,2,4-oxadiazol-idine-3,5-dione
46	metribuzin	125-126	4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
47	metsulfuron methyl	163-166	2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]-carbonyl]amino]sulfonyl]-benzoic acid, methyl ester
48	monuron	174-175	N'-(4-chlorophenyl)-N,N-dimethylurea
49	naptalam	185	2-[(1-naphthalenylamino)-carbonyl]benzoic acid
50	neburon	102-103	1-butyl-3-(3,4-dichloro-phenyl)-1-methylurea
51	nitralin	151-152	4-(methylsulfonyl)-2,6-dinitro-N,N-dipropyl-aniline
52	norflurazon	174-180	4-chloro-5-(methylamino)-2-[3-(trifluoromethyl)phenyl]-3(2H)-pyridazinone
53	oryzalin	141-142	4-(dipropylamino)-3,5-dinitro-benzenesulfonamide
54	perfluidone	142-144	1,1,1-trifluoro-N-[2-methyl-4-(phenylsulfonyl)phenyl]-methanesulfonamide
55	phenmedipham	143-144	3-[(methoxycarbonyl)amino]-phenyl (3-methylphenyl)-carbamate

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
56	picloram	>215 (DEC)	4-amino-3,5,6-trichloro-2-pyridinecarboxylic acid
57	prometryn	118-120	N,N'-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine
58	pronamide	155-156	3,5-dichloro-N-(1,1-dimethyl-2-propynyl)benzamide
59	propazine	212-214	6-chloro-N,N'-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine
60	pyrazon	205-206	5-amino-4-chloro-2-phenyl-3(2H)pyridazinone
61	siduron	133-138	N-(2-methylcyclohexyl)-N'-phenylurea
62	simazine	225-227	6-chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine
63	sulfometuron methyl	182-189	2-[[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]benzoic acid, methyl ester
64	tebuthiuron	161-164	N-[5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl]-N,N'-dimethylurea

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
65	terbacil	175-177	5-chloro-3-(1,1-dimethyl-ethyl)-6-methyl-2,4(1H,3H)-pyrimidinedione
66	terbuthyl-azine	177-179	2-(tert-butylamino)-4-chloro-6-(ethyl-amino)-s-triazine
67	terbutryn	104-105	N-(1,1-dimethylethyl)-N'-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine
68	triclopyr	148-150	[(3,5,6-trichloro-2-pyri-dinyl)oxy]acetic acid
69	2,4-D	140	(2,4-dichlorophenoxy)acetic acid
70	2,4-DB	119-120	4-(2,4-dichlorophenoxy)-butanoic acid
71	triasulfuron	>100	(3-(6-methoxy-4-methyl-1,3,5-triazin-2-yl)-1-[2-(2-chloroethoxy)phenylsulfonyl] urea
72	primisulfuron	>100	[2-/3-(4,6-bis(difluoro-methoxypyrimidin-2-yl-ureidosulfonyl)benzoic acid methylester]

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
73	----	>100	[2-/3-(4,6-bis(difluoro-methoxy)-pyrimidin-2-yl)-ureidosulfonyl)-benzoic acid methylester]
74	NC-311	170-172	[5-pyrazolesulfonamide, N-[(4-methoxy-6-methyl-pyrimidine-2-yl)-amino-carbonyl]-4-methoxy-carbonyl-1-methyl-]
75	----	160-162	N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-pyridinesulfonamide
76	----	152-159	2-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]-N,N-dimethyl-3-pyridine-carboxamide
77	----	204-206	Methyl 2-[[[[[4-ethoxy-6-(methylamino)-1,3,5-triazin-2-yl]amino]carbonyl]amino]-sulfonyl]benzoate

FUNGICIDES

78	carbendazim	302-307	methyl 2-benzimidazole-carbamate

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
79	thiuram	146	tetramethylthiuram disulfide
80	dodine	136	n-dodecylguanidine acetate
81	chloroneb	133-135	1,4-dichloro-2,5-dimethoxy-benzene
82	cymoxanil	160-161	2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide
83	captan	178	N-trichloromethylthiotetra-hydrophthalamide
84	folpet	177	N-trichloromethylthio-phthalimide
85	thiophanate-methyl	195	dimethyl 4,4'-(o-phenylene)-bis(3-thioallophanate)
86	thiabendazole	304-305	2-(thiazol-4-yl)benzimida-zole
87	chlorothalonil	240-241	tetrachloroisophthalo-nitrile
88	dichloran	195	2,6-dichloro-4-nitroaniline
89	captafol	160-161	cis-N-[1,1,2,2-tetrachloro-ethyl)thio]cyclohex-4-ene-1,2- dicarbioximide

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
90	iprodione	133-136	3-(3,5-dichlorophenyl)-N-(1-methylethyl)-2,4-dioxo-1-imidazolidine carboxamide
91	vinclozolin	108	3-(3,5-dichlorophenyl)-5-ethenyl-5-methyl-2,4-oxazolidinedione
92	kasugamycin	202-204 (DEC)	kasugamycin
93	triadimenol	121-127	beta-(4-chlorophenoxy)-α-(1,1-dimethylethyl)-1-H-1,2,4-triazol-1-ethanol
94	flutriafol	130	+-α-(2-fluorophenyl-α-(4-fluorophenyl)-1H-1,2,4-triazole-1-ethanol
95	flusilazol	52-53 HCl 201-203	1-[[bis(4-fluorophenyl)-methylsilyl)methyl]-1H-1,2,4-triazole
96	hexaconazole	111	(+/-)-α-butyl-α-(2,4-dichlorophenyl)-1H-1,2,4-triazole-1-ethanol
97	fenarimol	117-119	α-(2-chlorophenyl)-α(4-chlorophenyl)-5-pyridinemethanol

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
BACTERICIDES			
98	oxytetracycline dihydrate	181-182 (DEC)	oxytetracycline dihydrate
ACARICIDES			
99	hexathiazox	108-109	trans-5-(4-chlorophenyl)-N-cyclohexyl-4-methyl-2-oxo-3-thiazolidinecarboxamide
100	oxythioquinox	169-170	6-methyl-1,3-dithiolo-[2,3-B]quinonolin-2-one
101	dienochlor	122-123	bis(pentachloro-2,4-cyclo-pentadien-1-yl)
102	cyhexatin	245	tricyclohexyltin hydroxide
103	fenbutatin oxide	145	bis[tris(2-methyl-2-phenyl-propyl)tin] oxide
INSECTICIDES			
104	carbofuran	150-152	methylcarbamic acid, ester with 2,3-dihydro-2,2-di-methyl-7-benzofuranol
105	carbaryl	142	methylcarbamic acid, ester with a-naphthol

Cmpd. No.	Common Name	m.p.(°C)	Chemical Name
106	thiodicarb	173-174	dimethyl N,N'-[thiobis-(N-methylimmo)carbonyl-oxy]]-bis[ethanimido-thioate]
107	deltamethrin	98-101	α-cyano-3-phenoxybenzyl-cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane carboxylate
108	tetrachlorvinphos	93-98	(Z)-2-chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate

The compositions of this invention contain at least one water-soluble diluent. This is defined as a water-soluble polymer, salt, surfactant, hydrated organic or inorganic compound or carbohydrate which melts or softens at elevated temperatures and acts as the primary extrusion aid. It has been discovered that, in some cases, a suitable water-soluble diluent may have a melting point significantly higher than the extrusion temperature but it will nevertheless function as an effective extrusion aid. Apparently it forms a lower melting eutectic mixture with other soluble ingredients in the composition. For example, urea has a sharp melting point at 133°C which is higher than typical extrusion temperatures. Napthalene sulfonates and their condensates, which are well known in the art as dispersants and wetting agents for agricultural formulations, have no melting point. However, a mixture of the two in the presence of residual moisture in the composition, will soften at temperatures as low as 80°C making the urea an effective extrusion aid. Some non-limiting examples of suitable water-soluble diluents are hydroxyethylcellulose, sorbitol, lactose, urea, ethylurea, polyvinyl alcohol and sodium acetate trihydrate.

In a preferred embodiment, the compositions of this invention include a heat activated binder along with the water soluble diluent. The heat-activated binder (HAB) is a solid, surface active material which dissolves rapidly in water, has some viscosity near its melting point, and is capable of acting as a binder and extrusion aid when heat is applied. At an elevated temperature the binder softens and melts,

thereby becoming sticky enough to bind the pesticidal particles into larger aggregates. It is theorized that the softened or melted HAB can also function as a plastic or viscoelastic lubricant allowing the composition to extrude more easily through a die or screen. The preferred melting point range for the HAB is 45°C to 100°C. Examples of suitable HABs, which are not intended to be limiting, are ethylene oxide/propylene oxide copolymers, polyethoxylated alkylphenols, polyethoxylated fatty acids or alcohols and polyethylene glycol. Preferred HAB's are ethylene oxide/propylene oxide copolymers and polyethoxylated alkylphenols. Most preferred are block copolymers of ethylene oxide/propylene oxide where 80% is ethylene oxide and 20% is propylene oxide, and polyethoxylated dinonyl phenol with approximately 150 moles of ethylene oxide.

The composition also contains disintegrant(s) which wick in water and physically expand to aid break-up of the granule. Non-limiting examples of suitable disintegrants include starch, cross-linked polyvinylpyrrolidone, microcrystalline cellulose, cross-linked sodium carboxymethyl cellulose, sodium starch glycolate, soy polysaccharide and ion exchange resins. Cross-linked polyvinylpyrrolidone and cross-linked sodium carboxymethyl cellulose are preferred.

Dispersant(s) are needed to help disperse the active ingredient in water. Non-limiting examples of suitable dispersants include sodium and ammonium salts of napthalene sulfonate-formaldehyde condensates; sodium, calcium and ammonium salts of

ligninsulfonates (optionally polyethoxylated); sodium and ammonium salts of maleic anhydride copolymers and sodium salts of condensed phenolsulfonic acid.

Optional additives include:

(1) Anticaking agents to prevent clumping of granules when stored under hot warehouse conditions. Non-limiting examples include sodium and ammonium phosphates, sodium carbonate and bicarbonate, sodium acetate, sodium metasilicate, magnesium, zinc and calcium sulfates, magnesium hydroxide, (all optionally as hydrates), anhydrous calcium chloride, molecular sieves, sodium alkylsulfosuccinates, calcium and barium oxides.

(2) Chemical stabilizers to prevent decomposition of the active(s) during storage. Non-limiting examples of suitable chemical stabilizers include alkaline earth and transition metal sulfates such as magnesium, zinc, aluminum and iron; sodium hexametaphosphate, calcium chloride and boric anhydride.

(3) Gas producing disintegrants for faster breakup of the granule in water. Non-limiting examples of suitable gas generating additives are combinations of sodium and potassium bicarbonates and carbonates with acids such as citric and fumaric acid.

(4) Wetting agents to improve the speed of wetting upon mixing with water. Non-limiting examples of suitable anionic wetting agents include sodium salts of alkyl napthalene sulfonates, alkyl benzene sulfonates, alkyl sulfosuccinates, taurates, alkyl sulfates and phosphate esters. Examples of suitable nonionic wetting agents include acetylenic diols and alkyl phenol ethoxylates.

(5) Inert fillers, including but not limited to inorganic fillers well known in the art. Non-limiting examples are swelling and non-swelling clays, synthetic and diatomaceous silicas, calcium and magnesium silicates, titanium dioxide, aluminum, calcium and zinc oxide, calcium and magnesium carbonate, ammonium, sodium, potassium, calcium and barium sulfate, charcoal.

The granules of this invention beak up rapidly and form high quality dispersions in water as determined from the Long Tube Sedimentation test described in U.S. 3,920,442 col.9, lines 1 to 39. Acceptable Long Tube Sedimentation values correspond to 0.02 ml, preferably 0.01 ml of solids after 5 minutes of settling. The granules should exhibit low attrition characteristics which can be determined by the attrition test in U.S. 3,920,442 col 8, lines 5 to 48. The test is modified to use test samples of the appropriate granule size (e.g. 14-20 U.S. mesh). Attrition values of less than 40% and preferably less than 30% are acceptable.

The following examples are presented to illustrate, but not to restrict, this invention.

Identity of Ingredients Used in Examples

Name	Identity
Macol® DNP150 (Mazer Chemicals)	Polyethoxylated dinonylphenol (150 moles ethylene oxide)
Pluronic® F108 propylene (BASF Corp)	80% Ethylene oxide/20% oxide block copolymer

Identity of Ingredients Used in Examples

Name	Identity
Polyplasdone® XL-10 (GAF Corp)	Crosslinked polyvinyl pyrrolidone
Lomar® PWA (Henkel Corp)	Ammonium napthalene sulfonate-formaldehyde condensate
Morwet® EFW (Witco Corp)	Mixture of alkyl carboxylate and Sodium alkyl napthalene sulfonate

Example 1

A 150 gm premix was formulated from the ingredients listed below. The ingredients were blended and then passed through a MikroPulverizer hammer mill. The milled premix was slowly added to a 1 inch Wayne single screw extruder with a 25:1 L/D ratio. The extruder had three electrical heating zones along the barrel plus a band heater for the die. Temperatures were generally kept as uniform as possible along the barrel and the die. A mechanical or electronic pressure indicator was fitted near the end of the barrel to measure hydraulic pressures close to the die.

The premix was extruded through a die containing 8 x 1 mm holes arranged in a circular pattern. The extruded product was allowed to cool for a few minutes then it was chopped up in a small food processor and screened to obtain the 14 to 35 U.S. sieve cut size.

Extruder temperature range	87-91°C
Hydraulic pressure range	0 - 50 psi

Premix Formulation

	Weight Percent
Diuron technical	62.4
Lomar® PWA	10.0
Macol® DNP150	5.0
Morwet® EFW	2.0
Polyplasdone® XL-10	2.0
Urea	18.6

Properties of Granules	
Long Tube Sedimentation	.002
Long Tube Sedimentation after aging 2 weeks @ 54C	.002
% Attrition (14-20 mesh cut)	1.7
Bulk Density (lb/cu ft)	39.8

Example 2

The procedure of Example 1 was used with the following premix. The die had 6 x 1mm holes arranged in a hexagonal pattern.

Extrusion temperature range	88-94°C
Hydraulic pressure range	0-1000 psi

Premix Formulation

	Weight Percent
Diuron technical	62.4
Lomar® PWA	7.0
Pluronic® F108	5.0
Polyplasdone® XL-10	2.0
Citric acid anhydrous	2.0
Sodium bicarbonate	3.0
Urea	18.6

Properties of Granules

Long Tube Sedimentation	.002
Long Tube Sedimentation after aging 2 weeks @ 54C	trace
% Attrition (14-20 mesh cut)	8.7
Bulk Density (lb/cu ft)	25.1

Example 3

The procedure of example 2 was used with the following premix.

Extrusion temperature range	88-94°C
Hydraulic pressure range	300-500 psi
Screw speed	26 rpm

Premix Formulation

	Weight Percent
Diuron technical	62.4
Lomar® PWA	7.0
Macol® DNP150	5.0
Polyplasdone® XL-10	2.0
Citric acid anhydrous	5.0
Sodium carbonate anhydrous	4.0
Urea	14.6

Properties of Granules

Long Tube Sedimentation	trace
Long Tube Sedimentation after aging 2 weeks @ 54C	.002
% Attrition (14-20 mesh cut)	8.3
Bulk density (lb/cu ft)	23.9

Example 4

The procedure of example 2 was used with the following premix:

Extrusion temperature range	86-91°C
Hydraulic pressure range	100-300 psi
Screw speed	26 rpm

Premix Formulation

	Weight Percent
Diuron technical	62.4
Lomar® PWA	7.0
Macol® DNP150	5.0
Polyplasdone® XL-10	2.0
Citric acid anhydrous	5.0
Sodium carbonate anhydrous	4.0
Calcium sulfate anhydrous	3.0
Urea	11.6

Properties of Granules

Long Tube Sedimentation	0
Long Tube Sedimentation after aging 2 weeks @ 54C	.002
% Attrition (14-20 mesh cut)	6.7
Bulk density (lb/cu ft)	24.8

Example 5

The procedure of Example 2 was used with the following premix:

Extrusion temperature range	84-92°C
Hydraulic pressure range	100-300 psi
Screw speed	30 rpm

Premix Formulation

	Weight Percent
Methyl 2-[[[[(4-methyl-6-methoxy-1,3,5-triazin-2-yl)amino]carbonyl]amino]-sulfonyl]benzoate	52.0
Lomar® PWA	7.0
Pluronic® F108	8.0
Polyplasdone® XL-10	2.0
Citric Acid anhydrous	1.0
Sodium bicarbonate	1.5
Sorbitol	28.5

Properties of Granules

Long Tube Sedimentation	trace
Long Tube Sedimentation after aging 2 weeks @ 54C	.004
% Attrition (14-20 mesh cut)	0.7
Bulk density (lb/cu ft)	39.6

Example 6

The procedure of Example 2 was used with the following premix. 200 gm of premix was prepared for extrusion.

Extrusion temperature range	84-87°C
Screw speed	30 rpm

Premix Formulation

	Weight Percent
Methyl 2-[[[[(4-methyl-6-methoxy-1,3,5-triazin-2-yl)amino]carbonyl]amino]-sulfonyl]benzoate	52.0
Lomar® PWA	7.0
Pluronic® F108	8.0

Polyplasdone® XL-10	2.0
Citric acid anhydrous	1.0
Sodium bicarbonate	1.5
Type 4A molecular sieve (pulverized)	4.0
Sorbitol	24.5
Properties of Granules	
Long Tube Sedimentation	.002
Long Tube Sedimentation after 2 weeks @ 54°C	.003
Bulk density (lb/cu ft)	39.0

CLAIMS

What is claimed is:

1. Water dispersible granular compositions comprising by weight based on the total weight of the composition:

1) 0.01-90% of one or more active ingredients;
2) 1-60% of one or more water-soluble diluents;
3) up to 30% of one or more water-soluble heat activated binders that melt at temperatures between 40-120°C; and
4) two or more additives selected from the group consisting of:
   a) up to 0% anticaking agent(s);
   b) up to 10% chemical stabilizer(s);
   c) up to 20% gas generators;
   d) 0.1-10% disintegrant(s);
   e) 0.1-20% dispersant(s);
   f) up to 5% wetting agent(s); and
   g) up to 80% inert filler(s);

and the sum of all the ingredients in a composition is 100%.

2. The composition of Claim 1 wherein the active ingredient(s) comprise 10-70%, and the heat activated binder(s) comprise 1-15%.

3. The composition of Claim 2 wherein the heat activated binder(s) is selected from the group consisting of polyethoxylated dinonylphenol, ethylene oxide/propylene oxide copolymer and mixtures of the foregoing.

4. The composition of Claim 3 wherein the water soluble diluent is urea, ethylurea, sorbitol, lactose or sodium acetate trihydrate and mixtures thereof.

5. The composition of Claim 4 wherein the ethylene oxide/propylene oxide copolymer if present is about 80% ethylene oxide and 20% propylene oxide and the polyethoxylated dinonylphenol has 150 ethylene oxide units.

6. The composition of Claim 4 wherein the water soluble diluent is urea or sorbitol.

7. The composition of Claim 6 wherein the active ingredient is N'(3,4-dichlorophenyl)-N,N-dimethyl urea.

8. The composition of Claim 6 wherein the active ingredient is methyl 2-benzimidazole-carbamate.

9. The composition of Claim 6 wherein the active ingredient is selected from the group consisting of

methyl 2-[[[[(4,6-dimethyl-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]benzoate;

methyl 3-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate;

2-chloro-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]-benzene-sulfonamide;

ethyl 2-[[[[(4-chloro-6-methoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]benzoate;

methyl 2-[[[[(4-methyl-6-methoxy-1,3,5-triazin-2-yl)amino]carbonyl]amino]-sulfonyl]benzoate;

2-[[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]-N,N-dimethyl-3-pyridinecarboxamide;

methyl 2-[[[[[4-ethoxy-6-(methylamino-1,3,5-triazin-2-yl]amino]carbonyl]-amino]sulfonyl]benzoate;

methyl 2-[[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N-methylamino]carbonyl]amino]sulfonyl]benzoate;

methyl 2-[[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-methyl]benzoate;

N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl]-3-(ethylsulfonyl)-2-pyridine sulfonamide;

methyl 2-[[[[[4,6-bis(difluoro-methoxy)-2-pyrimidinyl]amino]carbonyl]-amino]sulfonyl]benzoate;

2-(2-chloroethoxy)-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl]-benzene sulfonamide;

ethyl 5-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methyl-1H-pyrazole-4-carboxylate; and

N-[[(4,6-dimethoxy-2-pyrimidinyl)amino]-carbonyl]-1-methyl-4-(2-methyl-2H-tetrazol-5-yl)-1H-pyrazole-5-sulfonamide.

10. A process comprising extruding a dry premix of the composition of any one of Claims 1-7 through a die or screen at a temperature from 50°C to 130°C to form granules.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/01262

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 A01N25/14

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	A01N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	US,A,4 065 289 (D.J.JUDD) 27 December 1977 cited in the application see column 1, line 25 - column 1, line 62 see column 2, line 54 - column 4, line 13; claims; examples	1,2,10
X	FR,A,2 645 709 (SUMITOMO CHEMICAL COMPANY LTD) 19 October 1990 see page 2, line 11 - page 2, line 21 see page 5, line 34 - page 6, line 17; claims; examples	1-6
P,X	WO,A,9 113 546 (E.I.DU PONT DE NEMOURS &CO.) 19 September 1991 see page 2, line 8 - page 3, line 15; claims; examples	1-3

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° Special categories of cited documents : [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
29 MAY 1992	12 JUN 1992
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	DONOVAN T.M.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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X	EP,A,0 256 608 (STAUFFER CHEMICAL COMPANY) 24 February 1988 see page 4, line 50 - page 7; claims; examples	1
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ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9201262 SA 58320

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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